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MATHÉMATIQUE

Sur la décomposition des nombres naturels en sommes de nombres triangulaires distincts

par

A. SCHINZEL

Présenté par W. SIERPIŃSKI le 24 Juin 1954

En 1949 H. E. Richert a démontré (voir [1], théorème 5) que tout nombre naturel > 33 est une somme de nombres triangulaires distincts > 0. Sa démonstration ne donne aucun moyen de prouver l'existence d'un nombre naturel m tel que tout nombre naturel suffisamment grand soit une somme de m ou de moins que m nombres triangulaires distincts.

Le but de cette note est de déduire de deux propositions démontrées en 1933 par G. Pall [2] ce

Théorème. *Tout nombre naturel* > 51 *est une somme de quatre nombres triangulaires distincts* ($\geqslant 0$).

Démonstration. G. Pall [2] a démontré deux propositions suivantes P_1 et P_2:

P_1. Les seuls nombres naturels qui ne sont pas des sommes de 4 carrés distincts $\geqslant 0$ sont les nombres $4^h a$, où $h = 0, 1, 2, \ldots$ et $a = 1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 23, 25, 27, 31, 33, 37, 43, 47, 55, 67, 73, 97, 103, 2, 6, 10, 18, 22, 34, 58, 82$.

P_2. Pour qu'un nombre impair a soit une somme de 4 carrés distincts $\geqslant 0$, il faut et il suffit que le nombre $4a$ soit une somme de quatre carrés distincts impairs.

Soit k un nombre naturel > 51. On a donc $2k+1 > 103$ et il résulte de la proposition P_1 que le nombre $2k+1$ est une somme de 4 carrés distincts $\geqslant 0$, ce qui entraîne, d'après la proposition P_2, que $8k+4$ est une somme de 4 carrés distincts de nombres impairs. On a donc

$$8k+4 = (2a+1)^2 + (2b+1)^2 + (2c+1)^2 + (2d+1)^2, \tag{1}$$

où a, b, c, d sont des entiers distincts $\geqslant 0$.

En posant

$$\frac{n(n+1)}{2} = t_n \quad \text{pour} \quad n = 0, 1, 2, \ldots,$$

on trouve tout de suite, d'après (1):

$$k = t_a + t_b + t_c + t_d,$$

ce qui prouve que k est une somme de 4 nombres triangulaires distincts $\geqslant 0$. Notre théorème se trouve ainsi démontré.

Remarques. Quant au nombre 51, on vérifie facilement qu'il n'est pas une somme de 4 nombres triangulaires distincts $\geqslant 0$; or, on a

$$51 = t_0 + t_3 + t_9 = t_0 + t_5 + t_8.$$

On démontre sans peine que les seuls nombres naturels qui ne sont pas des sommes de 4 nombres triangulaires distincts $\geqslant 0$ sont les nombres 1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 12, 13, 15, 16, 18, 21, 23, 27, 33, 36, 48 et 51, et les seuls nombres naturels qui ne sont pas des sommes de nombres triangulaires distincts sont les nombres 2, 5, 8, 12, 23 et 33.

Remarquons enfin que l'hypothèse exprimée par G. Pall ([2], p. 11): "It is conjectured, that every $2(8n+1)$ except 2 is a sum of three positive squares" — n'est pas vraie, puisque le nombre $2(8.8+1) = 130$ n'est pas une somme de trois carrés de nombres naturels.

Institut Mathématique de l'Université de Varsovie

OUVRAGES CITÉS

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MATHEMATICS

A Random Ergodic Theorem

by

S. GŁADYSZ

Presented by H. STEINHAUS on July 5, 1954

1. Let $(S, \mathcal{B}, m)$, $m(S)=1$, and $(X, \mathcal{E}, \mu)$, $\mu(X)=1$, be two measure spaces, T an $\mathcal{E}$-measurable and μ-preserving transformation of X into itself ($E \in \mathcal{E}$ implies $T^{-1}(E) \in \mathcal{E}$ and $\mu(T^{-1}(E))=\mu(E)$). Let $\Phi=\{\varphi_x | x \in X\}$ be a family of $\mathcal{B}$-measurable and m-measure preserving transformations φ_x of S into S. We suppose that the family Φ is $\mathcal{B}\times\mathcal{E}$-measurable [2].

All the theorems in this paper are given for the convergence almost everywhere, but they are also valid for convergence in L^p, $p \geqslant 1$.

I. *If* $f(s,x) \in L(S\times X)$ *then for* $(m\times\mu)$ *almost all* (s,x)

$$\lim_{n\to\infty} \frac{1}{n} \sum_{k=0}^{n} f(\varphi_{T^{k-1}x} \dots \varphi_{Tx}\varphi_x s, T^k x) = F(s,x) \in L(S\times X).$$

This generalization of the random ergodic theorem has also been obtained by C. Ryll-Nardzewski.

By a suitable choice of the measure space $(S, \mathcal{B}, m)$, of the family Φ and of the function $f(s,x)$ we obtain the following version of the ergodic theorem:

II. *If* $f(x) \in L(X)$, *and if* $q(x)$ *is a complex-valued measurable function such that*

$$|q(x)|=1,$$

then for μ*-almost all* x *exists the limit*

$$\lim_{n\to\infty} \frac{1}{n} \sum_{k=0}^{n} q(x)\cdot q(Tx)\cdot \dots \cdot q(T^{k-1}x)\cdot f(T^k x) = F(x) \in L(X).$$

The limit function $F(x)$ *fulfils a. e. the equation*

$$q(x)\cdot F(Tx) = F(x).$$

If the transformation T *is indecomposable (i. e. if every set invariant with respect to* T *is of measure* 0 *or* 1*) then a. e.*

$$|F(x)| = a = \text{const.}$$

and if $a \neq 0$ *then*

$$\int_X \frac{f(x)}{F(x)}\, d\mu = 1.$$

2. Set $(X_1, \mathcal{E}_1, \mu_1) = (X_2, \mathcal{E}_2, \mu_2) = \ldots = (X, \mathcal{E}, \mu)$ and denote by $(X_r^*, \mathcal{E}_r^*, \mu_r^*)$ the product of r measure spaces $(X, \mathcal{E}, \mu)$, i. e.

$$X_r^* = X_1 \times \ldots \times X_r, \qquad \mathcal{E}_r^* = \mathcal{E}_1 \times \ldots \times \mathcal{E}_r, \qquad \mu_r^* = \mu_1 \times \ldots \times \mu_r,$$

and by $(X^*, \mathcal{E}^*, \mu^*)$ the countable product

$$X^* = X_1 \times X_2 \times \ldots, \qquad \mathcal{E}^* = \mathcal{E}_1 \times \mathcal{E}_2 \times \ldots, \qquad \mu^* = \mu_1 \times \mu_2 \times \ldots$$

Let $\Phi_r = \{\varphi_{x_r^*} = \varphi_{(x_1,\ldots,x_r)} | x_r^* = (x_1, \ldots, x_r) \in X_r^*\}$ be a family of $\mathcal{B}$-measurable m-measure preserving transformations of S into S. Let us suppose that the family Φ_r is $\mathcal{B} \times \mathcal{E}_r^*$-measurable, i. e. for every $B \in \mathcal{B}$ we have

$$\{(s, x_r^*) | \varphi_{x_r^*} s \in B\} \in \mathcal{B} \times \mathcal{E}_r^*.$$

III. Random ergodic theorem. *If* $f(s; x_1, x_2, \ldots) \in L(S \times X^*)$, *if* $q(s; x_1, \ldots, x_r)$ *is* $\mathcal{B} \times \mathcal{E}_r^*$*-measurable and if*

$$|q(s; x_1, \ldots, x)| = 1,$$

then there exists a function $F(s; x_1, \ldots, x_{r-1}) \in L(S \times X_{r-1}^*)$ *such that for* $(m \times \mu^*)$*-almost all* (s, x^*)

$$\lim_{n\to\infty} \frac{1}{n} \sum_{k=0}^{n} [q(s; x_1, \ldots, x_r) \cdot \ldots \cdot q(\varphi_{(x_k,\ldots,x_{k+r-1})} \ldots \varphi_{(x_1,\ldots,x_r)} s; x_{k+1}, \ldots, x_{k+r}) \cdot$$
$$\cdot f(\varphi_{(x_{k+1},\ldots,x_{k+r})} \ldots \varphi_{(x_1,\ldots,x_r)} s; x_{k+2}, x_{k+3}, \ldots)] = F(s; x_1, \ldots, x_{r-1}).$$

For every natural r it is easy to give an example of a family Φ_r and a function $f(s, x^*) = g(s)$ depending on s only, so that for $q \equiv 1$ the limit function F essentially depends on each variable $s, x_1, \ldots, x_{r-1}$. Moreover, every transformation of the family Φ_r can be indecomposable.

For $r = 1$ and $q \equiv 1$ we obtain from III the known version of the random ergodic theorem ([2], [4], [5]):

III′. *If* $f(s) \in L(S)$, *then for* $(m \times \mu^*)$*-almost all* (s, x^*)

$$\lim_{n\to\infty} \frac{1}{n} \sum_{k=0}^{n} f(\varphi_{x_k} \ldots \varphi_{x_1} s) = F(s) \in L(S).$$

The proof of III is a modification of the method of Ryll-Nardzewski [5]. I use a known theorem of B. Jessen ([1], p. 23) concerning the integrals of a function defined in a countable product of spaces and the following

Lemma. *Let* $f(x) \in L(X)$ *and* $q(x)$ *an* $\mathcal{E}$*-measurable function with* $|q(x)| = 1$. *If for almost all* x *there exists*

$$\lim_{n\to\infty} q(x)\cdot\ldots\cdot q(T^{n-1}x)\cdot f(T^n x),$$

then for almost all x

$$q(x)\cdot f(Tx) = f(x).$$

3. An immediate connexion with the random ergodic theorem has the transformation

$$\varphi^*(s; x^*) = \varphi^*(s; x_1, x_2, \ldots) = (\varphi_{(x_1,\ldots,x_r)}s; x_2, x_3, \ldots),$$

defined on the product $S\times X^*$. We shall give the conditions of its indecomposability and mixing property.

The family Φ_r is called *indecomposable*, if every set $E^* \in \mathcal{B}\times\mathcal{E}^*_{r-1}$ almost invariant under μ_r-almost all transformations

$$\psi_{x_r}(s; x_1, \ldots, x_{r-1}) = (\varphi_{(x_1,\ldots,x_r)}s; x_2, \ldots, x_r)$$

is of $(m\times\mu^*_{r-1})$-measure 0 or 1.

IV. *The transformation* φ^* *is indecomposable if and only if the family* Φ_r *is indecomposable.*

The indecomposability of Φ_r is therefore a necessary and sufficient condition of every limit function F, for $q\equiv 1$ in III, being constant a. e.

The family Φ_r is called *mixing* if every proper function [3] of the transformations ψ_{x_r}, defined on $S\times X^*_{r-1}$, corresponding for μ_r-almost all x_r to the same proper value is constant a. e.

V. *The transformation* φ^* *has only trivial* (*constant a. e.*) *proper functions if and only if the family* Φ_r *is mixing.*

This theorem answers a question set by E. Marczewski concerning the mixing property of the transformation φ^*. It is worth noticing that there exists a mixing family such that all transformations belonging to it have a common proper value and even a common nontrivial proper function. Of course this nontrivial proper function does not correspond to the same proper value for almost all transformations.

The proofs and certain applications will be given elsewhere.

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MATHEMATICS

On a Topological Method for Studying the Behaviour of the Integrals of Ordinary Differential Equations

by

A. PLIŚ

Presented by T. WAŻEWSKI on July 9, 1954

In this note we give a generalization of a theorem of T. Ważewski ([1], Théorème p. 299) with some applications.

1. Notations and definitions. Let us suppose that the right-hand members of the system

$$\frac{dx_i}{dt} = f_i(t, x_1, \ldots, x_n) \qquad (i = 1, \ldots, n) \tag{1}$$

are defined and continuous on an open set $\Omega \subset E_{n+1}$ and that through every point P of Ω passes one and only one integral. We denote by t_P the projection of P on the t-axis (i. e. the first co-ordinate of the point P) and by X_P the projection of P on the hyperplane $(x_1, \ldots, x_n)$.

We put

$$Y(t, P) = (t, x_1(t, P), \ldots, x_n(t, P)),$$

where $x_i = x_i(t, P)$ $(i = 1, \ldots, n)$ is an integral of system (1) passing through the point P. It is known that the function $Y(t, P)$ is defined and continuous for $P \in \Omega$, $t \in \Delta(P)$, where $\Delta(P)$ is the maximal open interval in which exists the integral passing through P.

Let us denote by $L^+(P)$ the set of all points $Q = Y(t, P)$ for which $t \geqslant t_P$. Let ω be an open set which is contained in Ω. We say that the point $P \in \Omega B(\omega)$, where $B(\omega)$ denotes the boundary of ω, is the point of egress from ω (with respect to the system (1) and the set Ω), if there exists a positive number ε such that $Y(t, P) \in \omega$ for $t_P - \varepsilon < t < t_P$. If, moreover, there exists a positive number η such that $Y(t, P) \in \Omega - \overline{\omega}$ for $t_P < t < t_P + \eta$, the point P is called the point of strict egress from ω *). We denote by S the set of points of egress. If for the point $P \in \omega$ the relation $L^+(P) \subset \omega$ is not satisfied we denote by $C(P)$ such a point

*) These notions are due to T. Ważewski. See [1].

$Q = Y(\tilde{t}, P)$ that $Q \in \Omega B(\omega)$ and $Y(t, P) \in \omega$ for $t_P < t < \tilde{t}$. It is evident tha $C(P) \in S$.

We say that a set A is *a quasi-isotopic deformation retract* of a set B in the topological space E if there exists a continuous function $G(P, s)$ which maps the topological product $B \times I$, where I denotes the closed interval $[0, 1]$, into E and which fulfils the following conditions:

(2) $\quad G(P, 0) = P \quad$ for $\quad P \in B$

(3) $\quad G(P, s) = P \quad$ for $\quad P \in A, \quad 0 \leqslant s \leqslant 1$

(4) $\quad G(P, 1) \in A \quad$ for $\quad P \in B,$

(5) The transformation $H_s(P) = G(P, s)$ is a homeomorphism for $0 \leqslant s < 1$. (The transformation $H_1(P)$ is not supposed to be univalent on B) *).

2. Theorem. *Let us suppose that every point of egress from* ω *(with respect to the system* (1) *and the set* Ω*) is a point of strict egress and that certain sets* Z, S_1 *satisfy the following conditions:* $S_1 \subset S$, $Z \subset \omega + S_1$, $Z \neq 0$,

(6) S_1 *is not a quasi-isotopic deformation retract of* $Z + S_1$ *in* $\omega + S_1$.

Under these assumptions there exists a point $P_0 \in \omega Z$ *such that* $L^+(P_0) \subset \omega$, *or* $C(P_0) \in S - S_1$.

Proof. Suppose the theorem is false. Then $C(P) \in S_1$ for every $P \in \omega Z$. Hence we can define a transformation $K(P)$ in the following manner:

$$K(P) = P \quad \text{for} \quad P \in S_1$$
$$K(P) = C(P) \quad \text{for} \quad P \in \omega Z.$$

This transformation is continuous ([1], p. 298). Therefore

$$G(P, s) = Y((1 - s)t_P + s t_{K(P)}, P) \text{ **)}$$

is a continuous function on the topological product $(Z + S_1) \times I$ to $\omega + S_1$. The inverse function $H_s^{-1}(Q)$ $(0 \leqslant s < 1)$ of $H_s(P) = G(P, s)$ is also continuous, which is evident from the equality

$$H_s^{-1}(Q) = Y\left(\frac{1}{1 - s} t_Q - \frac{s}{1 - s} t_{K(Q)}, Q\right).$$

Hence the function $H_s(P) = G(P, s)$ is for $0 \leqslant s < 1$ a homeomorphism. It can easily be verified that the conditions (2), (3), (4) (for $A = S_1$, $B = Z + S_1$) are also satisfied. Therefore S_1 is a quasi-isotopic deformation retract of $Z + S_1$ in $\omega + S_1$. Thus our supposition has led to a contradiction of (6). This completes the proof.

3. Remark 1. The condition $L^+(P) \subset \omega$ was introduced by T. Ważewski in paper [1] as a geometrical analogue of classical asymptotic properties and the condition $C(P_0) \in S - S_1$ as an analogue of the classical

*) The notion of the quasi-isotopic deformation retract is closely related to the notion of deformation retract formulated by K. Borsuk in [2].

**) This function was used in the paper of F. Albrecht [3].

boundary condition *). In applications of the topological method of T. Ważewski to a concrete asymptotic problem, the set ω used to be matched in relation to the asymptotic condition (and to right-hand members of (1)).

Remark 2. Our theorem is also a generalization of a theorem of F. Albrecht ([3], Théorème 1). In the theorem of T. Ważewski ([1], p. 299) instead of assumption (6) there are two assumptions formulated with the help of the notion of the retract. In the theorem of F. Albrecht the notion of deformation retract was used in the hypothesis corresponding to our assumption (6).

Now we give a variant of an example from paper [1] (p. 282).

Example 1. Let the following system be given:

$$\dot{x}_1 = f_1(t, x_1, x_2)$$
$$\dot{x}_2 = f_2(t, x_1, x_2)$$

with properties of system (1) for $\Omega = E_3$ and ω defined by the inequalities: $-\infty < t < \infty, -1 < x_1 < 1, -1 < x_2 < 1$. Suppose the points satisfying $|x_1| = 1$, $|x_2| < 1$ are the point of strict egress and the points satisfying $|x_1| \leqslant 1$, $|x_2| = 1$ are not the points of egress. As the set Z we take the sum of four segments, two of them joining the point $(1, {}^1/_2, 0)$ with the points $(1, -1, {}^1/_2)$, $(1, -1, -{}^1/_2)$ and the other two the point $(1, -{}^1/_2, 0)$ with the points $({}^1/_2, 1, 0)$, $({}^3/_2, 1, 0)$. As the set S_1 we take the set $S(|x_1| = 1, |x_2| < 1)$.

The set $Z + S_1$ is a chain-like set consisting of two components (links). It can be verified that assumption (6) holds; hence, since the set $S - S_1$ is empty, there exists an integral passing through a point $P^* \in Z$ such that $L^+(P^*) \subset \omega$. The problem of the existence of such an asymptotic integral passing through some point of Z has been raised by T. Ważewski.

4. Remark 3. It is easy to observe that condition (6) is a consequence of the following property of sets S_1, Z, ω:

(6 bis) *There does not exist a continuous function* $F(P, s)$ *on* $Z \times I$ *to* $\omega + S_1$, *and such that* $F(P, 0) = P$ *for* $P \in Z, F(P, 1) \in S_1$ *for* $P \in Z$.

Hence if we replace (6) by (6 bis) our theorem remains true. It is clear that, unless $S_1 = 0$, the variant of our theorem with condition (6 bis) instead of (6), can be applied only when $\omega + S_1$ is not homeomorphic with a convex set.

5. Remark 4. It is known that in the case when the system (1) is dynamical, it is sufficient to consider the phase space without changing the formal content of the respective theorems.

*) In paper [1] are also included some examples of applications of topological method to both problems.

Now, making use of remarks 3 and 4, we give an example which is a variant of an example contained in paper [3].

Example 2. Given a dynamical system in the plane E_2 and two closed curves of Jordan Γ_1, Γ_2 ($\Gamma_1 \subset E_2, \Gamma_2 \subset E_2$) Γ_2 contained in the interior of the domain bounded by Γ_1, let all points of egress from the open domain D, bounded by the closed curves of Jordan Γ_1 and Γ_2 be the points of strict egress. Let us suppose that there are points on Γ_1 as well as on Γ_2 which are not the points of egress. Let Z be a closed curve of Jordan belonging to D such that the domain bounded by Z contains Γ_2. Let us put $S = S_1$, $\omega = D$. It is easy to observe that the sets S_1, Z, ω satisfy condition (6 bis). Hence there exists on the curve Z a point $\tilde{P}$ such that $L^+(\tilde{P}) \subset D$.

One can give analogous examples in the space E_3 for the interior ω_1 of an anchor-ring and for the interior ω_2 of the set bounded by two different concentric spherical surfaces. As to ω_1 we suppose e. g. that the points of egress form a set homeomorphic to the interior of a circle and as to ω_2, that neither of the spheres is contained in S. For ω_1 we take as $Z = Z_1$ e. g. a closed Jordan curve non-nullhomotopic in ω_1, and for ω_2 — the concentric spherical surface Z_2 contained in ω_2. There exists a point $P_1 \in Z_1 \omega_1$ (as well as $P_2 \in Z_2 \omega_2$) such that $L^+(P_1) \subset \omega_1$ ($L^+(P_2) \subset \omega_2$).

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MATHEMATICS

Characteristics of Non-linear Partial Differential Equations

by

A. PLIŚ

Presented by T. WAŻEWSKI on July 12, 1954

1. Let us suppose that the function $z(x,y)$ is of class C^1 in a neighbourhood of the point $(0,0)$ and satisfies in this neighbourhood a partial differential equation

$$z_x = f(x,y,z,z_y), \tag{1}$$

where the function $f(x,y,z,q)$ is of class C^1 in a neighbourhood of the point $(0,0,z(0,0),z_y(0,0))$.

Under these assumptions there exists a solution $\eta(x),\zeta(x),\gamma(x)$ of the characteristic equations (of (1))

$$\begin{aligned} \eta' &= -f_q(x,\eta,\zeta,\gamma) \\ \zeta' &= f(x,\eta,\zeta,\gamma) - \gamma f_q(x,\eta,\zeta,\gamma) \\ \gamma' &= f_y(x,\eta,\zeta,\gamma) + \gamma f_z(x,\eta,\zeta,\gamma) \end{aligned} \tag{2}$$

which fulfils the condition

$$\eta(0) = 0$$

(as well as the conditions $\zeta(0) = z(0,0)$ and $\gamma(0) = z_y(0,0)$) and in a certain neighbourhood of the point $x = 0$ the identities

$$\begin{aligned} \zeta(x) &= z\big(x,\eta(x)\big) \\ \gamma(x) &= z_y\big(x,\eta(x)\big) \quad *) \end{aligned} \tag{3}$$

Remark. In the classical formulation of this theorem the functions $f(x,y,z,q)$, $z(x,y)$ were supposed to be of class C^2. In the paper of T. Ważewski [1] the partial derivatives of $f(x,y,z,q)$ and $z(x,y)$ were supposed to satisfy the Lipschitz condition.

Proof **). Let us define an auxiliary family of functions

$$r_\delta(x,y) = \frac{f\big(x,y,z(x,y),\, z_y(x,y+\delta)\big) - f\big(x,y,z(x,y),\, z_y(x,y)\big)}{z_y(x,y+\delta) - z_y(x,y)} \tag{4}$$

in the case when $z_y(x,y+\delta) \neq z_y(x,y)$ and

$$r_\delta(x,y) = f_q\big(x,y,z(x,y),\, z_y(x,y)\big)$$

in the case when $z_y(x,y+\delta) = z_y(x,y)$.

*) This theorem was communicated on June 4, 1954 at the meeting of the Section of Differential Equations of the Institute of Mathematics, Polish Academy of Sciences.

**) The proof in [2] is not correct.

It is evident that there exist a positive number ε and a neighbourhood ω of $(0,0)$ such that the functions $r_\delta(x,y)$ are continuous in ω for $0<\delta<\varepsilon$ and that $r_\delta(x,y)\to f_q(x,y,z(x,y),z_y(x,y))$, as $\delta\to 0\,(\delta>0)$, uniformly in the set ω.

Now let us denote by $\eta_\delta(x)$ a solution of the equation

$$\eta' = -r_\delta(x,\eta)$$

satisfying the initial condition

$$\eta(0)=0. \tag{5}$$

It is obvious that the functions

$$\eta_\delta(x), \quad \zeta_\delta(x)=z(x,\eta_\delta(x)) \quad \text{and} \quad \gamma_\delta(x)=\big(z(x,\eta_\delta(x)+\delta)-z(x,\eta_\delta(x))\big)\delta^{-1}$$

fulfil the following system of equations

$$\begin{aligned}\eta' &= -f_q(x,\eta,\zeta,\gamma)+a_\delta(x,\eta)\\ \zeta' &= f(x,\eta,\zeta,\gamma)-\gamma f_q(x,\eta,\zeta,\gamma)+b_\delta(x,\eta)\\ \gamma' &= f_y(x,\eta,\zeta,\gamma)+\gamma f_z(x,\eta,\zeta,\gamma)+c_\delta(x,\eta),\end{aligned} \tag{6}$$

where

$$\begin{aligned}a_\delta(x,\eta) &= -r_\delta(x,\eta)+f_q\big(x,\eta,z(x,\eta),(z(x,\eta+\delta)-z(x,\eta))\delta^{-1}\big)\\ b_\delta(x,\eta) &= f\big(x,\eta,z(x,\eta),z_y(x,\eta)\big)-z_y(x,\eta)\,r_\delta(x,\eta)-\\ &\quad -f\big(x,\eta,z(x,\eta),(z(x,\eta+\delta)-z(x,\eta)\delta^{-1}\big)\\ &\quad +(z(x,\eta+\delta)-z(x,\eta))\delta^{-1}\cdot f_q(x,\eta,z(x,\eta),(z(x,\eta+\delta)-z(x,\eta))\delta^{-1}\big)\\ c_\delta(x,\eta) &= \delta^{-1}\big(f(x,\eta+\delta,z(x,\eta+\delta),z_y(x,\eta+\delta))-f(x,\eta,z(x,\eta),z_y(x,\eta))-\\ &\quad -(z_y(x,\eta+\delta)-z_y(x,\eta))\,r_\delta(x,\eta)\big)-f_y\big(x,\eta,z(x,\eta),(z(x,\eta+\delta)-z(x,\eta))\delta^{-1}\big)\\ &\quad -(z(x,\eta+\delta)-z(x,\eta))\,\delta^{-1}\cdot f_z\big(x,\eta,z(x,\eta),(z(x,\eta+\delta)-z(x,\eta))\delta^{-1}\big).\end{aligned}$$

It is evident that there exist a positive number α and a neighbourhood N of $x=0$ such that the functions $\eta_\delta(x)$, $\zeta_\delta(x)$, $\gamma_\delta(x)$ are uniformly bounded and equicontinuous in N for $0<\delta<\alpha$. Hence in virtue of a well known theorem there exists a sequence $\{\delta_m\}$ $\delta_m>0$, $\delta_m\to 0$ such that the sequences $\eta_{\delta_m}(x)$, $\zeta_{\delta_m}(x)$, $\gamma_{\delta_m}(x)$ are uniformly convergent on N to certain functions $\eta(x)$, $\zeta(x)$, $\gamma(x)$. It is clear that $\eta(0)=0$ and the identities (3) are satisfied in a neighbourhood of $x=0$.

It is easy to verify that the right-hand members of the system (6) tend in a neighbourhood of $(0,0,z(0,0)\,z_y(0,0))$ uniformly to the right-hand members of the system (2) as δ tends to zero, hence the functions $\eta(x)$, $\zeta(x)$, $\gamma(x)$ fulfil the system (2). This completes the proof.

2. Let us now consider the function $z(x,y_1,\ldots,y_n)$ of class C^1 in a neighbourhood of $x=0$, $y_k=0$ safisfying in this neighbourhood the equation

$$z_x = f(x,y_1,\ldots,y_n,z,z_{y_1},\ldots,z_{y_n}), \tag{7}$$

where the function $f(x, y_1, \ldots, y_n, z, q_1, \ldots, q_n)$ is of class C^1 in a neighbourhood of $x=0$, $y_k=0$, $q_k=0$ $(k=1, \ldots, n)$.

Under these assumptions there exists for every j $(j=1, \ldots, n)$ a solution $\eta_1^j(x), \ldots, \eta_n^j(x)$, $\zeta^j(x)$, $\gamma^j(x)$ of the system S^j of the form

$$\eta_i' = -f_{q_i}(x, \eta_1, \ldots, \eta_n, \zeta, \ldots, z_{y_{j-1}}(x, \eta_1, \ldots, \eta_n), \gamma, z_{y_{j+1}}(x, \eta_1, \ldots, \eta_n), \ldots,) \qquad (i=1, \ldots, n)$$

$$(8)\quad \zeta' = f(\ldots) - \gamma f_{q_j}(\ldots) - \sum_{\substack{k=1 \\ k\neq j}}^{n} z_{y_k}(x, \eta_1, \ldots, \eta_n) \cdot f_{q_k}(\ldots)$$

$$\gamma' = f_{y_j}(\ldots) + \gamma f_z(\ldots)$$

satisfying the initial conditions

$$(9)\quad \eta_i^j(0) = 0 \quad (i=1, \ldots, n) \quad \text{as well as} \quad \zeta^j(0) = z(0, \ldots, 0),\ \gamma^j(0) = z_{y_j}(0, \ldots, 0)$$

and in a neighbourhood of the point $x=0$ the identities

$$(10)\qquad \begin{aligned} \zeta^j(x) &= z(x, \eta_1^j(x), \ldots, \eta_n^j(x)), \\ \gamma^j(x) &= z_{y_j}(x, \eta_1^j(x), \ldots, \eta_n^j(x)). \end{aligned}$$

Under the additional assumption (assumption A) that the integral of the system

$$(11)\quad \eta_k' = -f_{q_k}(x, \eta_1, \ldots, \eta_n, z(x, \eta_1, \ldots, \eta_n), z_{y_1}(x, \eta_1, \ldots, \eta_n), \ldots, z_{y_n}(x, \eta_1, \ldots, \eta_n)) \qquad (k=1, \ldots, n)$$

passing through the point $x=0$, $\eta_k=0$ is unique, there exists a solution $\eta_1(x), \ldots, \eta_n(x)$, $\zeta(x)$, $\gamma_1(x), \ldots, \gamma_n(x)$ of the characteristic equations (of (7))

$$\eta_i' = -f_{q_i}(x, \eta_1, \ldots, \eta_n, \zeta, \gamma_1, \ldots, \gamma_n) \qquad (i=1, \ldots, n)$$

$$(12)\qquad \zeta' = f(\ldots) - \sum_{k=1}^{n} \gamma_k f_{q_k}(\ldots)$$

$$\gamma_i' = f_{y_i}(\ldots) + \gamma_i f_z(\ldots) \qquad (i=1, \ldots, n)$$

passing through the point $x=0$, $\eta_i=0$, $\zeta = z(0\ldots)$, $\gamma_i = z_{y_i}(0, \ldots, 0)$ and satisfying the identities:

$$(13)\qquad \begin{aligned} \zeta(x) &= z(x, (\eta_1(x), \ldots, \eta_n(x)) \\ \gamma_i(x) &= z_{y_i}(x, \eta_1(x), \ldots, \eta_n(x)) \qquad (i=1, \ldots, n) \end{aligned}$$

in a certain neighbourhood of $x=0$.

Proof. Using the notations $\beta_k = z_{y_k}(x, y_1, \ldots, y_n)$,

$$\beta_{k\delta}^j = z_{y_k}(x, y_1, \ldots, y_{j-1}, y_j + \delta, y_{j+1}, \ldots)$$

we define similarly to (4)

$$r_{i\delta}^j(x, y_1, \ldots, y_n) = \frac{f(x, y_1, \ldots, \beta_{i-1}, \beta_{i\delta}^j, \beta_{i+1,\delta}^j, \ldots,) - f(x, y_1, \ldots, \beta_{i-1}, \beta_i, \beta_{i+1,\delta}^j, \ldots)}{\beta_{i\delta}^j - \beta_i}$$

in the case when $\beta_{i\delta}^j \neq \beta_i$ and

$$r_{i\delta}^j(x, y_1, \ldots, y_n) = f_{q_i}(x, y_1, \ldots, y_n, z, x, y_1, \ldots, y_n, \beta_1, \ldots, \beta_{i-1}, \beta_i, \beta_{i+1,\delta}^j, \ldots \beta_{n\delta}^j)$$

in the case when $\beta_{i\delta}^j = \beta_i$.

Let us denote by $\eta_{1\delta}^j(x), \ldots, \eta_{n\delta}^j(x)$ a solution of the system of equations

$$\eta_i' = -r_{i\delta}^j(x, \eta_1, \ldots, \eta_n) \qquad (i = 1, \ldots, n)$$

satisfying the initial conditions

$$\eta_{i\delta}^j(0) = 0 \qquad (i = 1, \ldots, n).$$

The functions $\eta_{i\delta}^j(x)$, $\zeta_\delta^j(x) = z\big(x, \eta_{1\delta}^j(x), \ldots, \eta_{n\delta}^j(x)\big)$

$$\gamma_\delta^j(x) = \delta^{-1}\Big(z(x, \ldots, \eta_{j-1\delta}^j(x), \eta_{j\delta}^j(x) + \delta, \eta_{j+1\delta}^j(x), \ldots,) - z(x, \ldots, \eta_{j\delta}^j(x), \ldots,)\Big)$$

fulfil a system of equations

$$\eta_i' = -f_{q_i}\big(x, \eta_1, \ldots, z_{y_{j-1}}(x, \eta_1, \ldots, \eta_n), \gamma, z_{y_{j+1}}(x, \eta_1, \ldots, \eta_n), \ldots,\big) + a_{i\delta}^j(x, \eta_1, \ldots, \eta_n) \qquad (i = 1, \ldots, n)$$

$$\zeta' = f(\ldots) - \gamma f_{q_j}(\ldots) - \sum_{\substack{k=1 \\ k \neq j}}^{n} z_{y_k}(x, \eta_1, \ldots, \eta_n) \cdot f_{q_k}(\ldots) + b_\delta^j(x, \eta_1, \ldots, \eta_n) \tag{14}$$

$$\gamma' = f_{y_j}(\ldots) + \gamma f_z(\ldots) + c_\delta^j(x, \eta_1, \ldots, \eta_n)$$

having analogous properties to those of system (6). Namely, the right-hand members of (14) tend uniformly to the right-hand members of (8). Hence, there exists a solution $\eta_i^j(x), \zeta^j(x), \gamma^j(x)$ of (8) satisfying (9) and (10). It is evident that the functions $\eta_i^j(x)$ fulfil (11). Hence, under assumption A, the identities

$$\eta_i^j(x) = \eta_i^1(x) \qquad (i, j = 1, \ldots, n)$$

are satisfied. Then the functions $\eta_i(x) = \eta_i^1(x)$, $\zeta(x) = \zeta^1(x)$ and $\gamma_i(x) = \gamma^i(x)$ satisfy identities (13), equations (12), as well as the initial conditions $\eta_i(0) = 0$, $\zeta(0) = z(0, \ldots, 0)$, $\gamma_i(0) = z_{y_i}(0, \ldots, 0)$. This completes the proof.

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THEORETICAL PHYSICS

The Influence of Hindered Rotation on the Scattering of Slow Neutrons by Bound Protons

by
W. KOŁOS

Presented by L. INFELD on July 31, 1954

It has been shown in a previous paper [3] that the cross-section of a proton bound in a molecule having an additional degree of torsional freedom is given by*)

$$\sigma_{m_f\varrho_f m_i\varrho_i} = b_0^2 \sigma_{m_f m_i}. \tag{1}$$

Therefore, to get a result which may be compared with that obtained experimentally, we have to calculate

$$\sigma = \sum_{m_i} P_{m_i}\sigma_{m_i} = \sum_{m_i} P_{m_i} \sum_{m_f} b_0^2 \sigma_{m_f m_i}, \tag{2}$$

where P_{m_i} is the probability for the molecule to be initially in the state m_i, and the summation over m_f is limited by the law of conservation of energy.

For a transition $m_i \to m_f$ the differential cross-section of the proton will be given by the formula (1) from paper [3]. However, it may be shown (see also [4]) that when we consider the influence of rotation of a rigid molecule on the proton cross-section, the reduced mass factor μ^2 must be replaced by $(\mu_0\mu_1\mu_2\mu_3)^{1/2}$, where μ_i $(i = 1, 2, 3)$ are the principal values of the reduced mass tensor introduced by Sachs and Teller [6], and

$$\mu_0 = {}^1/_3 \sum_{i=1}^{3} \mu_i.$$

So, in Fermi's approximation, the differential cross-section of the proton being initially in the state m_i in a co-ordinate system with the z-axis in the direction of $\vec{k} = \vec{k}_i - \vec{k}_f$, will be given by

$$d\sigma_{m_i} = \frac{k_f \sigma_0 (\mu_0\mu_1\mu_2\mu_3)^{\frac{1}{2}}}{k_i \pi} \sum_{m_f} b_0^2 \left| \int U_{m_i}(\theta, \psi, \varphi) \cdot \right. \tag{3}$$

$$\left. \cdot \exp\{ik(c\cos\theta + a\sin\theta\sin\varphi)\} U^*_{m_i}(\theta, \psi, \varphi) \sin\theta \, d\theta \, d\psi \, d\varphi \right|^2 d\Omega,$$

*) For the notations used in this paper see [3].

where

$$U_m(\theta, \psi, \varphi) = \frac{1}{2\pi\sqrt{2 I_m}} t^{d/2} (1-t)^{s/2} F(m; t), \qquad t = \tfrac{1}{2}(1 - \cos\theta),$$

$$(4) \qquad I_m = \int_0^1 t^d (1-t)^s F^2(m; t)\, dt = \frac{1}{1+d+s+2p} \frac{p!(d!)^2 (s+p)!}{(d+s+p)!\,(d+p)!}$$

$$d = |\tau' - \tau|, \qquad s = |\tau' + \tau|,$$

$$F(m; t) = F(-p, 1+d+s+p, 1+d; t), \qquad p = 0, 1, \ldots$$

When the differences between the rotational levels of the scattering system are small compared to the neutron energy, which for thermal neutrons is fulfilled at least for low temperatures of the scattering medium, then the summation over m_f comprises very many terms. But it may be shown by numerical calculations (see also [5]) that the transition probabilities decrease rapidly for higher transitions, and the energy transferred to the proton will be small for all transitions with appreciable matrix elements. So, approximately, we may neglect the changes of the neutron energy due to the transitions of the system, the restricted sum over the final states in (3) may then be replaced by an unrestricted one and the summation carried out by closure. This is the "static approximation" of Placzek which, applied to formula (3) to perform the summation over j_f and τ_f', gives

$$(5) \qquad d\sigma_{m_i} = \frac{\sigma_0 (\mu_0 \mu_1 \mu_2 \mu_3)^{1/2}}{(2\pi)^4 I_{m_i}} \sum_{\tau_f} d\Omega\, b_0^2 \int_0^\pi |\Theta_{m_i}(\theta)|^2 \cdot$$

$$\cdot \exp\{i(\tau_i - \tau_f)\varphi - i(\tau_i - \tau_f)\varphi' + ika \sin\theta \sin\varphi + ika \sin\theta \sin\varphi'\} \sin\theta\, d\theta\, d\psi\, d\varphi\, d\varphi'.$$

Integrating in (5) over ψ, φ and φ' we get

$$(6) \qquad d\sigma_{m_i} = \frac{\sigma_0 (\mu_0 \mu_1 \mu_2 \mu_3)^{1/2}}{2\pi I_{m_i}} \sum_{\tau_f} d\Omega\, b_0^2 \int_0^\pi |\Theta_{m_i}(\theta)|^2 J_{\tau_{if}}^2 (ka \sin\theta) \sin\theta\, d\theta,$$

where for abbreviation we have written

$$\tau_{if} = \tau_i - \tau_f,$$

and $J_{\tau_{if}}(ka \sin\theta)$ is the usual Bessel function of order τ_{if}.

The square of the Bessel function may now be expanded in a power series and when we write the square of Jacobi's polynomials in the form

$$(7) \qquad F^2(m; t) = \sum_{m=0}^{2p} \gamma_m t^m,$$

then, integrating in (6) over t, we get for the differential cross-section:

$$(8)\qquad \left\{ \begin{aligned} d\sigma_{m_i} &= \frac{\sigma_0 (\mu_0 \mu_1 \mu_2 \mu_3)^{1/2}}{\pi I_{m_i}} \cdot \\ &\cdot \sum_{\tau_f} \sum_{n=0}^{\infty} b_0^2 \frac{(-1)^n (2\tau_{if}+2n)! (s+\tau_{if}+n)! (ka)^{2\tau_{if}+2n}}{n! (2\tau_{if}+n)! [(\tau_{if}+n)!]^2} \cdot \\ &\cdot \sum_{m=0}^{2p} \gamma_m \frac{(d+m+\tau_{if}+n)!}{(d+s+m+2\tau_{if}+2n+1)!} \, d\Omega, \end{aligned} \right.$$

and the total cross-section obtained from (8) may be written in the form:

$$(9)\qquad \sigma_{m_i} = \frac{4\sigma_0 (\mu_0 \mu_1 \mu_2 \mu_3)^{1/2}}{I_{m_i}} \sum_{\tau_f} \sum_{n=0}^{\infty}{}' \frac{(-1)^n D_{n+\tau_{if}}}{n! (2\tau_{if}+n)!},$$

where

$$(10)\qquad D_n = \frac{(2n)! (8\mu' E_i a^2/\hbar^2)^n (s+n)!}{(n!)^2} \sum_{m=0}^{2p}{}' \gamma_m \frac{(d+m+n)!}{(d+s+m+2n+1)!}.$$

Now we are able to calculate the cross-section of the proton bound in a methyl alcohol molecule. The molecule is assumed to be approximately a symmetric rotator. Some numerical values of the coefficients b_0^2 calculated assuming the value of the height of the potential barrier at 384 cm.$^{-1}$ [1], are given in the Table. They are average values for the three states arising through the threefold symmetry of the hindering potential.

TABLE

Transition $\tau_i \leftrightarrow \tau_f$	$0\leftrightarrow1$	$0\leftrightarrow3$	$0\leftrightarrow5$	$0\leftrightarrow7$	$0\leftrightarrow10$	$0\leftrightarrow1$	$0\leftrightarrow2$	$0\leftrightarrow3$	$0\leftrightarrow5$
b_0^2	0.995	0.959	0.88	0.80	0.63	0.919	0.719	0.488	0.15
	For the proton bound in the CH_3 group					For the proton bound in OH			

The cross-section of the total methyl alcohol molecule, assumed to be rigid (i. e., omitting the coefficient b_0^2 in (9)), as a function of the initial neutron energy, for the ground state as the initial state ($j=0, \tau'=0, \tau=0$), is shown in Fig. 1. We see there the contributions due to various changes of the quantum number τ, which must be multiplied by corresponding coefficients b_0^2 to give a cross-section calculated allowing for hindered rotation.

It must be remembered that in our approximation the proton cross-section depends only on the absolute value $|\tau_{if}|$, so that it is given by

$$(11)\qquad \sigma_{m_i} = \sigma_{m_i}(\tau_{if}=0) + 2\sum_{n=1}^{\infty} \sigma_{m_i}(\tau_{if}=n).$$

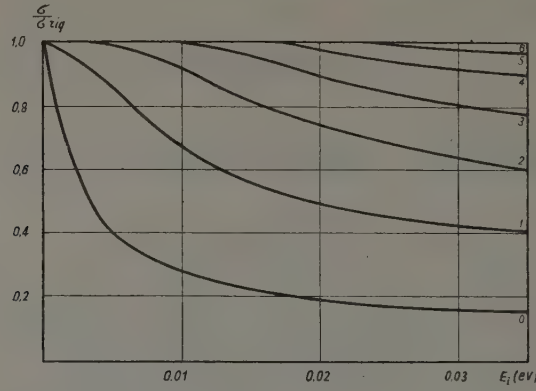

Fig. 1. Contributions to the total cross-section of the methyl alcohol molecule which is assumed to be rigid, due to various changes of the quantum number τ, for the initial state $j = 0$, $\tau' = 0$, $\tau = 0$. Curve o shows the elastic cross-section, curve p $(p = 1, 2...)$ shows the cross-section given by

$$\sigma_{m_i}^{(p)} = \sigma_{m_i}(\tau_{if} = 0) + 2\sum_{n=1}^{p} \sigma_{m_i}(\tau_{if} = n).$$

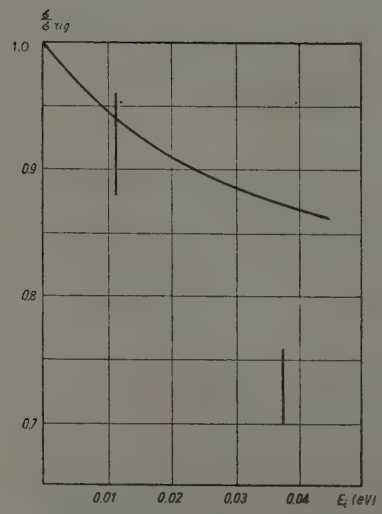

Fig. 2. Cross-section of the methyl alcohol molecule, averaged over the initial rotational states in units of the cross-section of the rigid molecule, as a function of the initial neutron energy. The vertical lines are the experimental results of Janik [2]

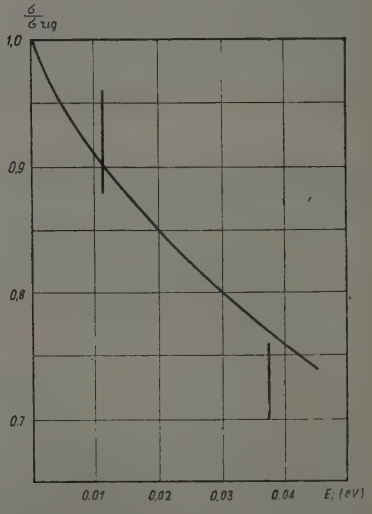

Fig. 3. Cross-section of the methyl alcohol molecule calculated, taking into account the influence of rotation and of hindered rotation, and assuming the influence of vibrations to be the same as for a methane molecule

To get a value of the cross-section which may be compared with that measured experimentally, we must apply formula (2), taking into account the statistical distribution of the molecules over the initial rotational states according to Boltzmann's statistics. The result of the calculations is shown in Fig. 2 and compared with experimental points found by Janik [2]. A Maxwell-like distribution is assumed for the neutrons with effective energy 3/2 kT. The calculated cross-section is only an elastic one with respect to the hindered rotation.

We see from Fig. 2 that the agreement with the experimental results is unsatisfactory. It must be remembered here that in the experiments of Janik the methyl alcohol was at room temperature, and the static approximation used in this paper holds better for lower temperatures of the scattering medium. But the principal reason of the discrepancy between the theoretical and experimental results may be found in our simplified model, neglecting vibrations of the protons. The lowest vibrational frequency of the protons in the CH_3 group of a methyl alcohol molecule is 1034 cm.$^{-1}$ [7]. For a methane molecule the lowest vibrational frequency of the protons is 1304 cm.$^{-1}$ [7], and for that molecule Messiah [4] has calculated the influence of vibration, rotation and translational motion on the cross-section. If we now assume the influence of vibrations on the cross-section of a methyl alcohol molecule to be the same as for a methane molecule we get a better agreement with the experimental results, as may be seen from Fig. 3.

However this agreement must be taken with some reserve on account of the rough estimation of the influence of vibrations, and of our model which, neglecting the influence of translational motion and association of the molecules in the liquid state, is still simplified.

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On Differential Structure of Non-local Field Theories

by
J. RZEWUSKI

Presented by L. INFELD on August 2, 1954

In the mathematical description of elementary particles non-local theories play an important rôle. The structure of these theories, however, is not yet fully clarified. The equations describing non-local systems are integro-differential and there arise questions concerning the manifold of solutions and the initial value problem.

In a preceding paper [1] it was shown on a simple example that an *ordinary* integro-differential equation (one independent variable) may be replaced by an equivalent purely differential equation of the same order in the derivatives. This enables one to apply the powerful analytical methods of the theory of differential equations to integro-differential equations and, in particular, to answer these questions.

In the present paper we shall study the practically important case of *partial* integro-differential equations describing non-local field theories.

Let us consider first the linear equation

$$(\Box - \varkappa^2)\, q(x) = \lambda \int_{\sigma_1}^{\sigma_2} K(x, x')\, dx'\, q(x'), \tag{1.1}$$

where x is a point of space-time, dx the four-dimensional volume element, and the integration domain is the region of space-time contained between two space-like surfaces σ_1 and σ_2. Units are chosen in which $\hbar = c = 1$. Equation (1.1) together with its complex conjugate describes a scalar charged field q, q^* interacting non-locally with a given external field, the interaction being contained in the kernel $K(x, x')$.

Theorem. *Equation* (1.1) *is equivalent with the equation*

$$(\Box - \varkappa^2)\, q(x) = -\lambda \int_{\sigma} A[\sigma](x, x')\, X'_\mu\, q(x')\, d\sigma'_\mu \tag{1.2}$$

in the sense that each solution of (1.1) *is a solution of* (1.2) *and vice versa, provided* λ *is sufficiently small and a certain kernel* $N(x, x')$ *is integrable.*

In (1.2) X_μ is a differential operator defined by

$$X_\mu = \vec{\partial}_\mu - \overleftarrow{\partial}_\mu, \tag{1.3}$$

the arrows indicating the direction in which the differentiations are to be carried out. The integral is taken over an arbitrary space-like surface σ, the quantity $A[\sigma](x, x')$ being a function of points x and x' and a functional of σ. The kernel $N(x, x')$ is given by the equation

$$N(x, x') = -\{GK\}(x, x'), \tag{1.4}$$

where $G(x)$ is an arbitrary particular solution of the equation

$$(\Box - \varkappa^2)\, G(x) = -\delta(x), \tag{1.5}$$

and where the notation

$$\{AB \dots C\}(x, x') = \int_{\sigma_1}^{\sigma_2} \dots \int_{\sigma_1}^{\sigma_2} A(x, \xi^1)\, d\xi^1\, B(\xi^1, \xi^2)\, d\xi^2 \dots d\xi^n\, C(\xi^n, x') \tag{1.6}$$

is used.

The proof of the theorem may be carried out by expansion of the right hand sides of (1.1) and (1.2) in powers of λ. One obtains the following recurrent formulae for the coefficients $A^{(n)}[\sigma](x, x')$ of the quantity $A[\sigma](x, x')$

$$\begin{aligned} A^{(n)}[\sigma(x')](x, x') &= -\{KN^n \Delta\}(x, x') - \\ &- \sum_{m=0}^{n-1} \int_{\sigma(x')} A^{(m)}[\sigma(x'')](x, x'')\, X''_\mu \{N^{n-m} \Delta\}(x'', x')\, d\sigma''_\mu. \end{aligned} \tag{1.7}$$

The notation $\sigma(x')$ indicates that σ is passing through point x'. Δ is the Jordan Pauli singular function defined by the three-dimensional Fourier-integral.

$$\Delta(x) = \frac{-1}{(2\pi)^3} \int d^3k\, e^{i\vec{k}\vec{x}} \frac{\sin \sqrt{\vec{k}^2 + \varkappa^2}\, x_0}{\sqrt{\vec{k}^2 + \varkappa^2}} \tag{1.8}$$

In virtue of the equation

$$\frac{\delta A[\sigma(x')](x, x')}{\delta \sigma(x'')} = \lambda A[\sigma(x'')](x, x'')\, A[\sigma(x')](x'', x') \tag{1.9}$$

which may be proved by induction, the right-hand side of equation (1.2) is independent of σ. This is necessary for the consistency of this equation. Choosing in particular σ through that point x which occurs as argument of the left-hand side of equation (1.2) we obtain an equation in which the unknown function q and its derivatives occur at points of one space-like surface only. Such an equation provides us with a description

of the system which is local in time, (although still non-local in the space-like directions due to the occurence of surface integrals).

Moreover, equation (1.2) gives immediately the solution of the initial value problem. Indeed, integrating (1.2) by means of $G(x)$, we obtain

$$q(x) = q^0(x) + \lambda \int_\sigma \{GA[\sigma]\}(x, x')\, X'_\mu\, q(x')\, d\sigma'_\mu, \tag{1.10}$$

where $q^0(x)$ is the general solution of the unperturbed ($\lambda = 0$) equation

$$(\Box - \varkappa^2)\, q^0(x) = 0, \tag{1.11}$$

and σ is again an arbitrary surface due to the property (1.9). In virtue of the relation

$$q^0(x) = \int_{\sigma_0} \Delta(x - x')\, X'_\mu\, q^0(x')\, d\sigma'_\mu \tag{1.12}$$

(σ_0 arbitrary) we may, by means of (1.10), express the solution q of equation (1.2) or (1.1) at a point x of the domain (σ_1, σ_2) by the initial values of q^0 and the normal derivative q^0_n at an arbitrary hypersurface σ_0 (in general not passing through x). To see this it is only necessary to choose the arbitrary particular solution G of equation (1.5) in such a way that it vanishes together with its first normal derivative for x on σ_0. In this case q and q_n coincide on σ_0 with q^0 and q^0_n respectively.

The values of $q^0(x)$ and $q^0_n(x)$ on σ^0 are arbitrary and, therefore, the manifold of solutions of (1.1) or (1.2) contains two arbitrary functions of three variables.

We may now proceed to the generalization of the above results to the case of non-linear equations. Take e. g. the non-local and non-linear system

$$\begin{aligned} (\Box) - \varkappa^2)\, \psi(1) &= \lambda \int_{\sigma_1}^{\sigma_2} P(1,2)\, \tilde{\varphi}(2)\, \tilde{\psi}(2)\, dx_2, \\ (\Box - m^2)\, \varphi(1) &= \lambda \int_{\sigma_1}^{\sigma_2} F(1,2)\, \tilde{\psi}(2) \tilde{\psi}(2)\, dx_2 \end{aligned} \tag{1.13}$$

where

$$\tilde{\psi}(1) = \int_{\sigma_1}^{\sigma_2} dx_2\, \psi(2)\, P^*(2,1), \quad \tilde{\varphi}(1) = \int_{\sigma_1}^{\sigma_2} dx_2\, \varphi(2)\, F(2,1). \tag{1.14}$$

The arguments $1, 2, 3, \ldots$ denote points $x^1_\mu, x^2_\mu, x^3_\mu, \ldots$ in space-time. The form factors P and F are functions of x^1_μ and x^2_μ by means of the invariant $(x^1_\mu - x^2_\mu)^2$ in order to secure translational and rotational invariance. Equations (1.13) correspond to the case of a charged scalar field ψ, ψ^* interacting non-locally with a neutral scalar field φ.

Theorem: *The set* (1.13) *is equivalent with the following set*

$$
\begin{aligned}
&(\Box - \varkappa^2)\,\psi(1) = \lambda \int\limits_{\sigma}\int A_1(1_3^2)\, X_\mu^2 X_\nu^3 \varphi(2)\,\psi(3)\, d\sigma_\mu^2\, d\sigma_\nu^3 + \\
&+ \lambda^2 \int\limits_{\sigma}\int\int [A_{21}\left(1_{\,3\,4}^{\,2}\right) X_\mu^2 X_\nu^3 X_\varrho^4 \psi^*(2)\,\psi(3)\,\psi(4) + \\
&+ A_{22}\left(1_{\,3\,4}^{\,2}\right) X_\mu^2 X_\nu^3 X_\varrho^4 \varphi(2)\,\varphi(3)\,\psi(4)]\, d\sigma_\mu^2\, d\sigma_\nu^3\, d\sigma_\varrho^4 + \\
&+ \ldots\ldots\ldots \\
&(\Box - m^2)\,\varphi(1) = \lambda \int\limits_{\sigma}\int B_1(1_3^2)\, X_\mu^2 X_\nu^3 \psi^*(2)\,\psi(3)\, d\sigma_\mu^2\, d\sigma_\nu^3 + \\
&+ \lambda^2 \int\limits_{\sigma}\int\int B_2\left(1_{\,3\,4}^{\,2}\right) X_\mu^2 X_\nu^3 X_\varrho^4 \psi^*(2)\,\varphi(3)\,\psi(4)\, d\sigma_\mu^2\, d\sigma_\nu^3\, d\sigma_\varrho^4 + \\
&+ \ldots\ldots\ldots
\end{aligned}
\tag{1.15}
$$

in the sense that each solution of (1.13) *is a solution of* (1.15) *and vice versa, provided* λ *is sufficiently small and* P *and* F *satisfy certain integrability conditions.*

The coefficients $A_1, A_{21}, A_{22}, \ldots B_1, B_2, \ldots$ may be calculated to any desired order of approximation. It is, of course, impossible to give closed recurrent formulae. We quote the results for the lowest approximations

$$
\begin{aligned}
A_1(1_3^2) &= \left\{P \begin{matrix}\widetilde{\Delta}_m \\ \widetilde{\Delta}_\varkappa^*\end{matrix}\right\}(1_3^2) \\
A_{21}\left(1_{\,3\,4}^{\,2}\right) &= \left\{P \begin{matrix}L & \widetilde{\Delta}_\varkappa \\ \widetilde{\Delta}_\varkappa^* & \widetilde{\Delta}_\varkappa^*\end{matrix}\right\}\left(1_{\,3\,4}^{\,2}\right) - \int\limits_{\sigma} A_1(1_4^5) X_\mu^5 \left\{\widetilde{G}_m \begin{matrix}\widetilde{\Delta}_\varkappa \\ \widetilde{\Delta}_\varkappa^*\end{matrix}\right\}(5_3^2)\, d\sigma_\mu^5 \\
A_{22}\left(1_{\,3\,4}^{\,2}\right) &= \left\{P \begin{matrix}\widetilde{\Delta}_m & \widetilde{\Delta}_m \\ K & \widetilde{\Delta}_\varkappa^*\end{matrix}\right\}\left(1_{\,3\,4}^{\,2}\right) - \int\limits_{\sigma} A_1(1_5^2) X_\mu^5 \left\{\widetilde{G}_\varkappa \begin{matrix}\widetilde{\Delta}_m \\ \widetilde{\Delta}_\varkappa^*\end{matrix}\right\}(5_4^3)\, d\sigma_\mu^5 \text{ etc.}
\end{aligned}
\tag{1.16}
$$

and similarly for $B_1, B_2, \ldots$ The symbol $\{\}$ has a meaning closely analogous to (1.6), e. g.

$$
\left\{P \begin{matrix}L & \widetilde{\Delta}_\varkappa \\ \widetilde{\Delta}_\varkappa^* & \widetilde{\Delta}_\varkappa^*\end{matrix}\right\}\left(1_{\,3\,4}^{\,2}\right) = \int\limits_{\sigma_1}^{\sigma_2} dx_5 \int\limits_{\sigma_1}^{\sigma_2} dx_6\, P(1,5)\, \widetilde{\Delta}_\varkappa^*(5,4)\, L(5,6)\, \widetilde{\Delta}_\varkappa^*(6,3)\, \widetilde{\Delta}_\varkappa(6,2). \tag{1.17}
$$

The functions $\Delta_\varkappa$ and Δ_m are defined by (1.8), the second one with m in place of $\varkappa$. $L, K, \widetilde{G}_m, \widetilde{G}_\varkappa, \widetilde{\Delta}_m, \widetilde{\Delta}_\varkappa$ are given by

$$
\begin{aligned}
&L = \{F^{tr} G_m F\},\ K = \{P^{tr} G_\varkappa P\}, \\
&\widetilde{G}_m = \{G_m F\},\ \widetilde{G}_\varkappa = \{G_\varkappa P\},\ \widetilde{\Delta}_m = \{\Delta_m F\}, \\
&\widetilde{\Delta}_\varkappa = \{\Delta_\varkappa P\},
\end{aligned}
\tag{1.18}
$$

where

$$
F^{tr}(1,2) = F(2,1),\ P^{tr}(1,2) = P(2,1), \tag{1.19}
$$

and G_m and $G_\varkappa$ are arbitrary particular solutions of equation (1.5), the first one with m in place of $\varkappa$.

The right-hand sides of (1.15) are independent of σ due to certain properties of the coefficients $A_1, A_{21}, \ldots B_1, B_2, \ldots$ analogous to (1.9). Choosing in particular σ through x we obtain a set of equations in which the unknown functions and their derivatives occur at points of one space-like surface only. Such equations provide us with a description of the system which is local in time. Analogously with the linear case we obtain the solution of the initial value problem integrating (1.15) by means of a properly chosen particular solution of (1.5).

It may be noted that the equivalence of equations (1.13) and (1.15) shows an interesting correspondence between non-local (1.13) and *essentially* non-linear (1.15) problems. We understand by essential non-linearity that e. g. in the equation for ψ (first equation (1.15)), ψ itself occurs non-linearly.

A detailed account of the above considerations will be given elsewhere.

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CHEMISTRY

Electrothermal Diffusion Method of Determining the Soret Coefficients in Aqueous Solutions of Copper Sulphate

by

B. BARANOWSKI and J. DEMICHOWICZ

Communicated by M. ŚMIAŁOWSKI at the meeting of June 21, 1954

The Soret coefficient is defined as the ratio of the coefficient of thermal diffusion D' to the coefficient of normal diffusion D. It can, for the stationary state, be expressed by means of the following correlation:

$$D'/D = d\ln n/dt,$$

where n denotes concentration and t - temperature. This magnitude expresses the degree of separation, caused by thermal diffusion, of liquid mixtures.

The thermo-gravitational method of determining Soret's factor is encumbered with a considerable experimental error due to the difficulty in assembling the apparatus, the chief element of which consists of two parallel walls spaced by tenths of a millimetre and maintained at varying temperatures. The fact that the distance between the walls occurs, in the formulae from which Soret's factor is computed, in the fourth power, accounts for the main source of error in this method.

The electrothermal diffusion method, which is a variation of the thermal gravitation method, is exempt from this source of error, since the upright, parallel walls have been replaced by a thin-walled glass capillary tube [1], [2]. The rôle of the cold wall is here performed by the wall of the capillary tube, water-cooled on the outside. The hot wall is superseded by a system of heating the capillary tube on the inside, by means of alternating current.

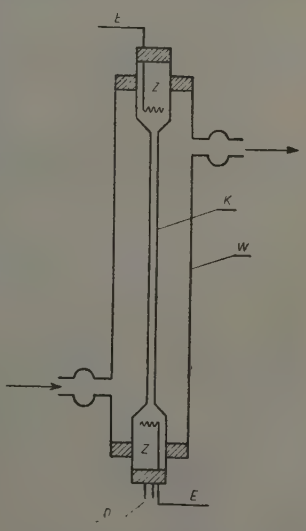

Fig. 1. — K — capillary tube, W — water jacket, E — electrodes, Z — supplementary vessels, O — opening

This method can, for this reason, be used solely in the case of electrolytic solutions or other liquid conductors.

The apparatus, shown diagrammatically in Fig. 1. and described above [1], [2], has been constructed in the following manner. The capillary tube, approximately 12 cm. long and with a radius of roughly 0.3—0.4 mm. uniform throughout its length and measured with an accuracy of up to 10^{-4} cm., was supplemented by two containers with a capacity of roughly 0.4 cu. cm. The complete assembly is water-jacketed. Copper electrodes were introduced into both supplementary vessels — top and bottom. The capillary tube was, together with the containers, filled with a copper sulphate solution through which alternating current at 1000 - 4000 V and a frequency of 50 cycles was then passed for 2 hours.

The concentrations in both supplementary vessels were, after the current had been cut off, determined by interferometer. The ratio of the concentrations in the top and bottom containers (n_D/n_G), the intensity of the current (i), the voltage drop in the capillary tube (U), the time length of current (τ) the length of the capillary tube (h_0), its inside radius (r_0) and the volume of one container (V) — all being known, the Soret factor was computed from the following formulae derived from the phenomenological theory of the electrothermal diffusion process [3]:

$$\frac{n_D}{n_G} - 1 = \frac{2\pi r_0^4 (\Delta t)^2 g\left(\beta\varrho + \frac{D'}{D} n_0 \alpha\right)\frac{D'}{D}\tau}{516\eta V} \tag{1}$$

$$\frac{n_D}{n_G} - 1 = \frac{\pi r_0^4 A^2 a^2 \frac{D'}{D} g\left(\beta\varrho + \frac{D'}{D} n_0 \alpha\right)\tau\left(1 - \frac{a}{20}\right)}{4608\eta V\left[1 - \frac{D'}{D} A\left(1 - \frac{a}{8} + \frac{a^2}{192}\right)\right]}. \tag{2}$$

The difference in temperature between the axis and wall of the capillary (Δt) was computed, for formula (1), from the relation:

$$\Delta t = \frac{\lambda M}{4\pi h_0 k} \tag{3}$$

and for formula (2) from the relation:

$$\Delta t = \frac{\lambda M\left(1 - \frac{a}{16}\right)}{4\pi h_0 k\left(1 - \frac{a}{8} + \frac{a^2}{192}\cdots\right)} = \frac{Aa}{4}\left(1 - \frac{a}{16}\right). \tag{4}$$

The values A and a were computed from the following formulae:

$$A = \frac{\lambda M}{2\pi h_0 k \sqrt{a} J_1(\sqrt{a})}, \tag{5}$$

$$a = \frac{\lambda U^2 \varkappa c r_0^2}{h_0^2 k}. \tag{6}$$

Notation of symbols used in the above formulae:

$\frac{1}{\lambda}$ — electric equivalent of heat;
M — power of current;
k — coefficient of thermal conductivity;
η — coefficient of viscosity;
β — temperature coefficient of density variation;
ϱ — density;
n_0 — initial (normal) concentration;
α — density derivative relatively to concentration;
$\varkappa$ — specific conductance of the solution;
c — temperature coefficient of specific conductance;
$J_1(\sqrt{a})$ — Bessel's function of the first kind and first order.

The temperature relation of conductance was ignored in compiling formula (1), but was duly allowed for in formula (2).

Mean results from not less than 2 measurements are given in Tables I and II below.

TABLE I

$\frac{n_D}{n_G}-1$	M Wat	$r\cdot10^2$ cm.	h_0 cm.	V cm.^{3}	Δt (4)	$\frac{D'}{D}\cdot10^3$ (1)	$\frac{D'}{D}\cdot10^3$ (2)
0.071	14.4	3.8	12.78	0.34	17.6	8.5	5.3
0.12	17.9	3.8	12.78	0.34	22.1	8.9	5.3
0.33	27.2	3.8	12.78	0.34	34.5	9.8	5.3
0.14	17.4	3.6	11.69	0.37	23.6	10.5	6.0
0.24	17.9	4.3	10.80	0.46	26.7	9.7	5.5
0.08	14.1	3.6	11.69	0.37	18.9	9.9	5.9
0.12	14.3	4.3	12.12	0.37	18.5	8.6	5 3
0·20	18.0	4.3	12.12	0.37	23.6	8.7	5.2
0.57	27.5	4.3	12.12	0.37	37.0	9.9	5.2

Table I summarises the results of measurements for 1 N $CuSO_4$, readings having been taken by varying the dimensions of the capillary tube (i. e. radius, length and capacity of containers) and voltage.

Table II contains the results for $CuSO_4$ solutions of varying concentration, and at definite other parameters (4).

It follows from the numeric values in the tables that Soret's coefficient does not depend on the power input; neither does it, virtually, depend on $CuSO_4$ concentration ranging from 0.1 to 1 N. A slight increase in the Soret coefficient was noticeable at a concentration of roughly 0.5, whereas it revealed, at a concentration of 0.05, a distinct decline.

TABLE II

n_0	$\frac{n_D}{n_G}-1$	M Wat	Δt (4)	$\frac{D'}{D}\cdot 10^3$ (1)	$\frac{D'}{D}\cdot 10^3$ (2)
0.75	0.077	14.4	16.4	8.8	5.8
0.75	0.130	17.9	20.4	9.3	5.7
0.50	0.072	14.2	16.2	9.8	6.1
0.50	0.130	17.9	20.4	11.0	6.4
0.25	0.046	14.6	16.7	8.0	5.6
0.25	0.089	17.8	20 3	9.8	5.7
0.10	0.053	14.7	16.8	11.0	5.9
0.10	0.071	18.0	20.5	9.9	5.4
0.05	0.031	14.4	16.4	7.5	4.5
0.05	0.051	17.8	20.3	8.0	4.1

Tables I and II show, for the sake of comparison, the values of Soret's coefficients computed from both formulae (1) and (2). The values computed from formula (2) are however, since they were obtained from the more accurate formulae, of paramount interest. The values of Soret's coefficients obtained by the electrothermal diffusion method are smaller than those obtained by hitherto prevalent methods [5], [6], [7]. This may be atributable to the influence of the electric field and to the likelihood of occurence of "current-diffusivity effect".

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CHEMISTRY

Phenomenological Theory of the Electrothermal Diffusion Method in Fluids

by

B. BARANOWSKI

Communicated by M. ŚMIAŁOWSKI at the meeting of June 21, 1954

Preamble

The Clusius thermogravitational method has been modified for liquid electrolyte solutions in the following manner: a thin-walled, cylindrical glass capillary tube [1], [2] was substituted for the customary two walls which have to be maintained at different temperatures. Two electrodes were fitted — one at the top and the other at the bottom — to which, after the capillary tube had been filled with an electrolyte solution, high alternating voltage was applied. The Joule heat produced inside the capillary tube produces a horizontal temperature gradient with which is associated the thermal diffusion flux. The convection current concurrently setting up in the capillary tube transfers the component, enriched in the axis of the capillary tube, to the container fitted at the top of the latter, and the component concentrated close to the wall of the capillary tube — to the container at the bottom of the capillary tube. This device, which has no hot wall and makes possible the application of the thermal diffusion process in the presence of an external electric field, has proved serviceable in the testing of binary and ternary mixtures [1], [2]. This method has been termed the "electrothermal diffusion method".

The phenomenological thermal gravitation theories in fluids hitherto published [3], [4], [5] could not, as a result of the different course taken by the temperature gradient (vide formula (2)) and different symmetry (the instance under reference herein reveals a cylindrical symmetry, whereas the Debye and de Groot theories apply to flat symmetry), be applied in this instance.

I hereunder present the phenomenological theory of the electrothermal diffusion method as advanced by me for small capillary tube radii and which provides an opportunity for making use of the Wirtz simplification [4]. A more detailed reference is given elsewhere [6].

Temperature gradient and maximum temperature difference in the capillary tube

Assuming temperature to be merely a function of distance from the axis of the capillary tube, we derive a Bessel's equation of the zero order expressing heat conductivity for the stationary state:

$$\frac{d^2z}{du^2}+\frac{1}{u}\frac{dz}{du}+z=0, \tag{1}$$

where:

$$z=at+b;$$

$$u=\sqrt{a}\xi;$$

$$a=\frac{\lambda U^2 \varkappa c r_0^2}{h_0^2 k};$$

$$b=\frac{\lambda U^2 \varkappa r_0^2}{h_0^2 k}(1-ct');$$

$$\xi=\frac{r}{r_0}.$$

Notation of symbols used:

$\frac{1}{\lambda}$ — electric equivalent of heat;
t — temperature;
U — voltage applied to the capillary tube;
$\varkappa$ — specific conductance at temperature t';
c — temperature coefficient of specific conductance;
r_0 — inside radius of capillary tube;
h_0 — height of capillary tube;
k — specific thermal conductivity;
r — common radius.

Integration of equation (1) leads, in making use of the lack of heat sources on the wall of the capillary tube, to the following formulae for temperature gradient and temperature difference between the inner wall of the capillary tube and its axis (Δt):

$$\frac{dt}{du}=-AJ_1(u), \tag{2}$$

$$\Delta t=\frac{Aa}{4}\left(1-\frac{a}{16}\right), \tag{3}$$

where

$$A=\frac{\lambda M}{2\pi h_0 k\sqrt{a}J_1(\sqrt{a})};$$

M — denoting the active power of the current;
$J_1(\sqrt{a})$ — Bessel's function of the first order.

In formula (3), $J_0(\sqrt{a})$ has been developed to the fourth term which is, since the value of "a" is small, adequate. The temperature gradient is, as will be appreciated from formula (2), dependent on the radius, whereas it was, according to the Debye and de Groot method [3], [5], independent of the co-ordinate.

Velocity of the convection current in the capillary tube

The Navier-Stokes equation will, after differentiation relatively to r and transformation to the variable u for the stationary state, take the following form:

$$\eta \frac{d}{du}\left[\frac{1}{u}\frac{d}{du}\left(u\frac{dV_h}{du}\right)\right] = \frac{gr_0^2}{a}\frac{d\varrho}{du}, \tag{4}$$

where η denotes the coefficient of viscosity;
V_h — the velocity of the convection current;
g — acceleration of gravity;
ϱ — density.

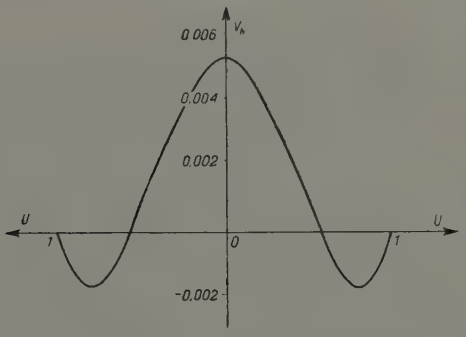

Fig. 1. $B=1$; $a=1$; V_h in B units when $a=1$.

Integration of equation (4) results, with vanishing of the convection current on the wall of the capillary tube and the lack of the resultant flux. in the following formula:

$$V_h = \frac{B}{16}\left(-\frac{u_0^2u^2}{3}+\frac{u^4}{4}+\frac{u_0^4}{12}\right), \tag{5}$$

where

$$B = \frac{gr_0^2A}{a\eta}\left[\beta\varrho+\frac{D'}{D}n_0\alpha\right];$$

β — denoting the temperature coefficient of density variation;
D'/D — Soret's factor;
n_0 — initial concentration of the electrolyte;
α — coefficient of density changes with concentration.

Bessel's functions have been developed into a power series up to the fourth term. The velocity of the convection current in the capillary tube corresponding to formula (5) is shown in Fig. 1.

Concentration changes in the containers

By making use of the Hiby and Wirtz simplification [4] relating to lack of influence of the convection current upon the stationary equilibrium in horizontal direction, we obtain the following formula for the flow of mass m during the time τ from one container to the other:

$$m = 2\pi\tau \int_0^{r_0} r V_h n \, dr. \tag{6}$$

Taking n as a function of radius in Fick's developed diffusion law for the stationary state [3], we derive the following expression for the ratio of concentrations n_D/n_G in the bottom and top containers

$$\frac{n_D}{n_G} = \frac{n_0 - \frac{m}{V}}{n_0 + \frac{m}{V}} \approx 1 - \frac{2m}{n_0 V} = 1 + \frac{2\pi r_0^4 (\Delta t)^2 g \tau \left[\beta\varrho + \frac{D'}{D} n_0 \alpha\right] \frac{D'}{D} \left(1 - \frac{\alpha}{20}\right)}{576 \eta V \left[1 - \frac{D'}{D} A \left(1 - \frac{\alpha}{8} + \frac{\alpha^2}{192}\right)\right] \left(1 - \frac{\alpha}{8}\right)}, \tag{7}$$

where V denotes the volume of one container.

The formula obtained may be useful in determining, by the electrothermal diffusion method, the Soret coefficients [7]. It follows from a comparison of formula (7) with the Hiby and Wirtz formula, that the ratio of concentrations in the case of the electrothermal diffusion method is, failing temperature relation in electric conductivity, higher by 20 per cent than in the case of the usual thermal gravitational method.

The ratio of concentrations under the electrothermal diffusion method is, at $a \sim 2$ — a value achievable under experimental conditions — higher by 50 per cent than in the case of the thermal gravitational method.

I desire to express my indebtedness to Professor K. Gumiński, K. Florek and D. Gutkowa, for their valuable advice, recommendations and criticism.

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CHEMISTRY

Properties of KCl Crystals Containing Metallic Thallium Centres. Photoelectric Effect

by

J. ROHLEDER

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Introduction

Alkali halide crystals with *F*-centres introduced by diffusion or taken up by some known method were the object of numerous investigations, mainly those of R. W. Pohl and his collaborators. Investigations were carried out to a much smaller extent on crystals, containing simultaneously very small amounts of foreign metal ions and *F*-centres. On the basis of the differences of the ionisation energy of foreign metal atoms and alkali metal atoms one might expect that the free electrons of the crystal would first concentrate in the close neighborhood of the foreign metal ions. The introduction of alkali metal atoms into crystals containing heavy metal ions would then lead to the appearance of new centres with photoelectric activity. This hypothesis was confirmed in only one of the cases investigated: a description was given of the photoelectric properties of KCl and NaCl crystals with metallic copper centres, probably of colloidal structure. The centres were introduced into the crystals by diffusion from Cu-electrodes [1].

In this study the subjects of investigations were KCl-TlCl crystals treated at higher temperatures with potassium vapour. The crystals were grown from a melt by the *Kyropoulos* method on a quartz rod cooled by flowing air. The TlCl content of the crystals was determined by the colorimetric method [2].

Small specimens of crystals were then enclosed under vacuum in glass rods with a small amount of twice-distilled potassium. The rods were placed for a few hours in an electric furnace at 550 - 600° C. When the diffusion process was finished the rods were cooled rapidly to room temperature: the crystals were taken out of the rods and subsequently placed in

a vacuum furnace at 550-600° C. The aim of this operation was to remove the excess of potassium atoms and to obtain crystals containing metallic thallium centres only. The operation of removing the excess of potassium atoms took about 6 hours. After cooling to room temperature the coloration of the crystals was a uniform yellow-brown one. A sample of $3\times3\times5$ mm. was cut out of the crystal and, after setting the aquadag electrodes on the 3×3 mm. opposite surfaces, the sample was placed in a vacuum apparatus for making the measurements.

Experimental work

The investigated crystal was placed in a vacuum apparatus in order to remove the surface conductivity of the sample. During the whole time of measurements a diffusion mercury pump was operating in order to keep the pressure in the apparatus at about 10^{-5} mm. Hg. The crystal was illuminated by tungsten-arc lamp radiation, distributed spectrally by a single monochromator. The voltage applied was received from a condenser of $1\,\mu F$ capacity charged before each measurement by means of a lamp rectifier. The photoelectric current was measured with a Wulf-electrometer, sensistivity about 20 mV/dash, using the time-measurements-method [3].

The values of the observed photocurrent lay in the region of $6\cdot10^{-14}$—$2\cdot10^{-12}$ A. Calculating the photocurrent flowing through the crystal at the given applied field E and at uniform illumination, we took into account the "dark current" flowing through the crystal while the illumination was shut out. After each measurement of the photoelectric current the voltage was switched off and the crystal was "illuminated" by infra-red radiation to remove the polarisation of the sample. This procedure of measurements assured a good reproductivity of results.

Results and discussion

Figure 1 shows the relationship between the photoelectric current i in arbitrary units and intensity of incident light I in arbitrary units for a crystal containing $4\cdot10^{-3}$ mol % Tl (crystal "1"). Figure 2 shows the relationship between photoelectric charge Q which flowed in 1 sec. and the applied field E. Crystal "1" was illuminated by undistributed radiation. The incident energy was estimated at 10^{-3} cal./cm.^{2} sec.

The linear dependence of photoelectric current on the intensity of incident light and on the applied field, and also the observation that the photoelectric current began immediately after the illumination was started and ceased simultaneously with the interruption of illumination, led to the supposition that a *primary* photoelectric current was observed.

Figure 3 shows the spectral distribution of the photoelectric current reduced to equal intensity of incident light*). Curve a refers to a crystal

*) The spectral distribution of the light source was separately measured by means of a specialy built Bi-BiPb vacuum-thermocouple [4].

containing $1.7 \cdot 10^{-2}$ mol % Tl (crystal "2"); curve *b* refers to a crystal containing $4 \cdot 10^{-3}$ mol % Tl (crystal "3"). In both cases a maximum was

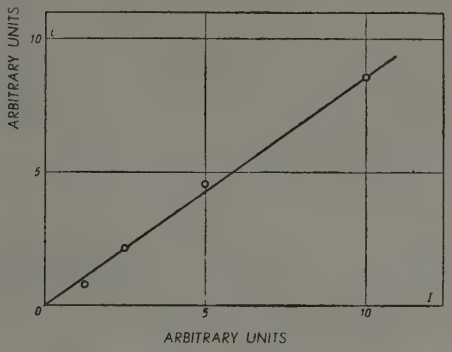

Fig. 1. Crystal "1", $4 \cdot 10^{-3}$ mol % Tl
$E = 7750$ V/cm., $\lambda = 702$ mμ

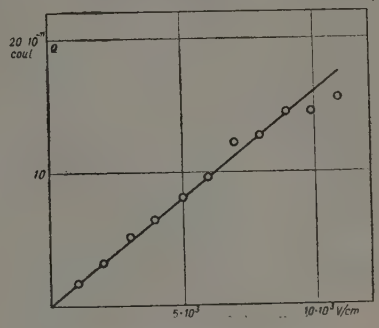

Fig. 2. Crystal "1", $4 \cdot 10^{-3}$ mol % T
Incident energy about
10^{-3} cal./cm.² sec.

observed in the spectral distribution for $\lambda_{max} = 550 \pm 20$ mμ corresponding to an optical energy of activation of 2.26 ± 0.08 eV.

When the excess of potassium atoms was not removed from the crystal, then — as other experiments showed — a different spectral distribution was observed (see Fig. 3, curve *c*). In this case there are two maxima: one about 820 mμ and the other at 510 mμ.

The photoelectric properties of the crystals described should be correlated with the existence of metallic thallium centres in the crystals. These centres are formed by thallium ions, which have caught electrons from potassium atoms introduced additively into the crystal. These centres have an atomic rather than a colloidal structure.

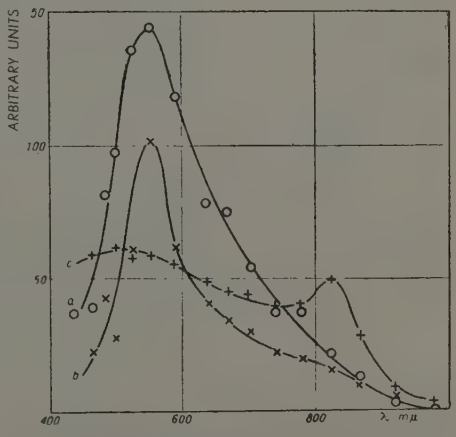

Fig. 3. Curve *a*: crystal "2", $1.7 \cdot 10^{-2}$ mol % Tl.
Curve *b*: crystal "3", $4 \cdot 10^{-3}$ mol % Tl.
Curve *c*: crystal "4", with excess of potassium atoms, $4 \cdot 10^{-3}$ mol % Tl

This view is supported by the marked differences between the localisation of the spectral distribution maxima of the observed photoeffect (550 ± 20 mμ) and the external photoeffect from the thallium surface (240 mμ). These differences are in contradiction with the normally observed approximate values of the internal effect maximum in the case of colloidal par-

ticles (for instance, for colloidal Na in NaCl, $\lambda_{max} = 365\,m\mu$ [5]) and of the external photoeffect from the surface of the corresponding metal (for instance, for Na surface, $\lambda_{max} = 340\,m\mu$ [6]). A further argument which appeals for an atomic structure of the Tl centres are the results of W. Koch's [7] dispersion investigations: they show that at not too high concentrations the Tl^+ ions are atomically dispersed in the KCl:TlCl crystals. It is not very probable that, during the heating, there took place a coagulation process of the Tl^+ ions.

More precise argumentation for these conclusions would require further investigations.

The author wishes to thank Professor K. Gumiński for continuous interest in this work.

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CHEMISTRY

Kinetics of Permanganate Reduction by OH^- Ions

by

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Communicated by W. TRZEBIATOWSKI at the meeting of June 21, 1954

Our earlier investigation [1] showed the radical character of the reduction of potassium permanganate with concentrated solution of KOH which proceeds in three consecutive stages at considerably different velocities:

$$Mn^{VII} \rightarrow Mn^{VI} \rightarrow Mn^{V} \rightarrow Mn^{IV}.$$

The purpose of the present work was to elucidate the mechanism of the reduction by finding the kinetic equations of the consecutive reactions.

The reactions were carried out in presence of an excess of OH^- ions which gave a constant ionic strength of the solution and enabled this reaction to be regarded as pseudo-unimolecular.

The differences of velocities of every reduction stage were increased considerably by an appropriate choice of the temperature and concentration parameters. The progress of each reaction was determined iodometrically in acid medium with 1/100 N solution of $Na_2S_2O_3$. For every determination, a separate solution was prepared to avoid errors in determination of oxidation states of manganese. These errors may result from the precipitation of MnO_2. The temperatures were held stable ($\pm 0.1^0$ C.).

The order of every consecutive reaction was determined by the half-life method.

The measurements of the rate of the $Mn^{VII} \rightarrow Mn^{VI}$ reaction were carried out at temperatures of -20^0 and 0^0 C. To determine the order of the reaction the process was slowed down by the use of 7 M KOH solution.

The experimental data followed the half-order equation:

$$\frac{dx}{dt} = k \frac{a - x}{x^{1/2}}$$

The formation of free OH radicals in this reaction stage was confirmed. The reduction of $KMnO_4$ was carried out in a saturated solution of $Ba(OH)_2$, in presence of benzene [2], well purified. In order to increase

the concentration of diphenyl, the same benzene was used in 5 succesive runs. Miligramme-order amounts of diphenyl were isolated from benzene and identified by determining the melting point (63° C.).

TABLE I

13.8 M/L KOH

$1.6 \cdot 10^{-3}$ M/L $KMnO_4$, temp. — 20° C.			$3.3 \cdot 10^{-3}$ M/L $KMnO_4$, temp. 0° C.		
t sec.	extent of conversion	$k/[MnO_4^-]_0^{1/2}$	t sec.	extent of conversion	$k/[MnO_4^-]_0^{1/2}$
6	0.37	0.0323	10	0.76	0.0831
20	0.65	0.0309	15	0.84	0.0862
30	0.77	0.0323	20	0.90	0.0863
45	0.86	0.0315	30	0.96	0.0862
	$k_m = 1.26 \cdot 10^{-3}$			$k_m = 4.90 \cdot 10^{-3}$	
		$E = 9.3$ kcal			
		7 M/L KOH, temp. 0° C.			
15	0.43	0.0171	15	0.39	0.0142
30	0.65	0.0206	30	0.57	0.0145
45	0.79	0.0232	45	0.69	0.0157
60	0.88	0.0260	60	0.77	0.0161
75	0.91	0.0242	75	0.83	0.0165
90	0.95	0.0265	90	0.86	0.0157
	$k_m = 9.16 \cdot 10^{-4}$			$k_m = 8.78 \cdot 10^{-4}$	

The kinetic equation which was found, and the experimentally stated existence of radicals may be attributed to the following mechanism:

$$MnO_4^- + OH^- = MnO_4^{=} + {}^{\cdot}OH$$
$$MnO_4^- + OH^- + {}^{\cdot}OH = MnO_4^{=} + H_2O + O$$
$$O + OH^- \rightleftarrows HO_2^-$$
$$MnO_4^- + HO_2^- + OH^- \rightleftarrows MnO_4^{=} + O_2^- + H_2O$$
$$MnO_4^- + O_2^- \rightarrow MnO_4^{=} + O_2$$

The first two reactions determine the speed of the reaction, the following ones explain the rôle of atomic oxygen, which diminishes the reaction order. The application of the stationary state hypothesis leads to the expression:

$$\frac{d[MnO_4^{=}]}{dt} = k\frac{[MnO_4^-]}{[O]^{1/2}}.$$

Irreversibility of the last reaction has been confirmed by carrying out the reaction in oxygen at a pressure of 1 — 15 atm. Independence of the velocity from pressure was found.

Recently, Symons [3], investigating the reaction of decomposition of $KMnO_4$ by NaOH solution, also assumed the formation of OH and other radicals. He supposed, that permanganate was not transiently reduced beyond the manganate stage: this is inconsistent with our experiments.

The measurements of the rate of reduction $Mn^{VI} \rightarrow Mn^{V}$ were carried out at the same concentration and at temperatures of -10^0 and 0^0 C. The further reduction of Mn^{V} to Mn^{IV} may be neglected, because of the stability of hypomanganate at low temperature [4]. The experimental data follow the same equation as in case of the reduction of $Mn^{VII} \rightarrow Mn^{VI}$, i. e. the half order equation, showing the similar mechanism of the process.

The existence of free OH radicals was confirmed by reducing $KMnO_4$ in 13.8 M KOH solution. The benzene was added on disappearance of Mn^{VII} and the mixture was stirred until complete transition of manganate into MnO_2. In the same way as before diphenyl was isolated.

TABLE II

13.8 M/L KOH, temp. 0° C.

$1.6 \cdot 10^{-3}$ M/L $KMnO_4$			$3.3 \cdot 10^{-3}$ M/L $KMnO_4$		
t min.	extent of conversion	$k/[MnO_4^{2-}]_0^{1/2}$	t min.	extent of conversion	$k/[MnO_4^{2-}]_0^{1/2}$
1	0.14	0.0370	1	0.11	0.0257
2	0.20	0.0335	2	0.16	0.0235
3	0.26	0.0346	4	0.24	0.0229
4	0.30	0.0332	6	0.30	0.0224
5	0.34	0.0316	8	0.36	0.0232
6	0.37	0.0325	10	0.42	0.0247
7	0.40	0.0316	12	0.45	0.0235
8	0.43	0.0322	13	0.48	0.0235
10	0.49	0.0334			
	$k_m \cdot 60 = 1.33 \cdot 10^{-3}$			$k_m \cdot 60 = 1.36 \cdot 10^{-3}$	
$1.6 \cdot 10^{-3}$ M/L $KMnO_4$, temp. -10^0 C.					
1	0.08	0.0150	5	0.21	0.0144
2	0.13	0.0165	6	0.23	0.0140
3	0.16	0.0156	7	0.26	0.0150
4	0.19	0.0152	9	0.32	0.0165
	$k_m \cdot 60 = 0.61 \cdot 10^{-3}$			$E = 11.2$ kcal.	

Measurements of the reduction rate $Mn^{V} \rightarrow Mn^{IV}$ were made in the same concentration and at temp. $+20^0$ and $+30^0$ C.

The reduction of Mn^{VII} and Mn^{VI} was shortened to a few minutes by increasing the temperature. The experimental data follow the kinetic equation

of — 1 order:

$$\frac{dx}{dt} = k\frac{a-x}{x^2}$$

hence

$$\frac{-d[MnO_4^{3-}]}{dt} = k\frac{[MnO_4^{3-}]}{[Mn^{IV}]^2}.$$

TABLE III

13.8 M/L KOH, temp. +20° C.

$1.6\cdot10^{-3}$ M/L $KMnO_4$			$3.3\cdot10^{-3}$ M/L $KMnO_4$		
t min.	extent of conversion	$k/[MnO_4^{3-}]_0^2$	t min.	extent of conversion	$k/[MnO_4^{3-}]_0^2$
30	0.43	0.00130	30	0.27	0.000266
60	0.50	0.00111	60	0.33	0.000266
120	0.61	0.00120	120	0.41	0.000275
180	0.65	0.00104	180	0.47	0.000290
240	0.69	0.00105	240	0.50	0.000278
300	0.72	0.00097	300	0.52	0.000266
	$k_m\cdot60 = 2.82\cdot10^{-9}$			$k_m\cdot60 = 2.91\cdot10^{-9}$	
13.8 M/L KOH, temp. + 30° C.					
60	0.39	0.00046	240	0.57	0.00046
120	0.50	0.00050	300	0.60	0.00042
180	0.54	0.00050	360	0.63	0.00046
	$k_m\cdot60 = 5.07\cdot10^{-9}$			$E = 23.0$ kcal	

This proves that the mechanism changes in the third reduction stage:

1) $MnO_4^{3-} + OH^- = MnO_4^{4-} + {}^{\cdot}OH$

2) $MnO_4^{4-} + 2H_2O \rightleftarrows MnO_2 + 4OH^-$.

The reduction reaction (1) is associated with an equilibrium (2). Each ion of MnO_4^{4-} is simultaneously attacked by two molecules of water producing MnO_2. The retarding influence of MnO_2 was confirmed by further experiments. The concentration of the OH radicals can be neglected according to Selwood's reaction of H_2O_2 decomposition [5] on the surface of MnO_2.

In order to investigate the influence of manganite in the reduction of hypomanganate with OH^- ions, the reduction of $1.6\cdot10^{-3}$ M/L $KMnO_4$ in 13.8 M/L KOH into Mn^{IV} was carried out and then the solution of Na_3MnO_4 was added. At the same time the sodium hypomanganate of the same concentration ($2.4\cdot10^{-2}$ M/L) was reduced in the KOH solution of the same molarity containing no MnO_2.

The measurements of the rates in these two simultaneous tests showed a distinct inhibition of the process in samples containing MnO_2.

The existence of free radicals in this reaction stage was shown by the reduction of sodium hypomanganate in 13.8 M/L KOH solution in presence of well purified benzene and by continuous stirring. Diphenyl was isolated as before.

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CHEMISTRY

Reactions of Aromatic Amines with Cyanguanidine. Formation of Derivatives of Amidineurea and Their Reaction with Aniline

by

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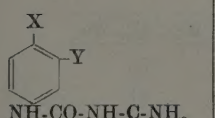
Presented by T. URBAŃSKI at the meeting of June 21, 1954

By means of the method described previously [1], consisting in boiling the corresponding aromatic amines with cyanguanidine in presence of hydrochloric acid, the following derivatives of N_1-amidine-N_2-phenylurea were prepared (Table I):

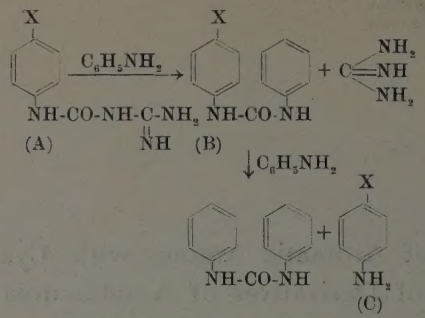
TABLE I



Compound	Name	X	Y	m. p.
I	*T* 222	Cl	H	143—144° C.
II	*T* 259	Br	H	172—173° C.
III	*T* 261	NH_2	H	300° C. (hydrochloride)
IV	*T* 221	SO_3H	H	267—269° C.
V	*T* 285	SO_2NH_2	H	212—213° C.
VI	*T* 325	H	OH	220—222° C. (sulphate)

The compound V was formed from the hydrochloride of p-sulphanilamide, in aqueous medium, without addition of hydrochloride acid, thus in conditions differing from those of preparation of other analogous compounds.

To complete the previous paper [1], the mechanism of the reaction between the derivatives of N_1-amidine-N_2-phenylurea (A) and aniline has been examined. It was now found that in the first instance an asymmetric urea derivative (B) and guanidine were formed. This, on further boiling in aniline, formed symmetric diphenylurea (carbanilide) and the corresponding amine (C). The first stage of the reaction was very rapid and sometimes the product (B) could not be isolated.



When repeating the reaction between N_1-amidine-N_2-(p-carboxyphenyl)-urea (i. e. $X = COOH$, $Y = H$) and aniline, we confirmed the mechanism described above and have stated that no decarboxylation of the compound (A) or (B) had occurred, contrary to the suggestion reported previously [1]. By interrupting the reaction in the early stage, it was possible to isolate compound (B) ($X = COOH$). Prolonged boiling in aniline led to formation of carbanilide and p-aminobenzoic acid.

Products I—VI have been examined *in vitro* from the viewpoint of their bacteriostatic action against Mycobacteria by S. Ślopek from the Silesian School of Medicine (Table II):

TABLE II

Compound	Name	Inhibiting concentration mg. %		
		Myc. 279	*Myc. smegmatis*	*Myc.* H_{37} *Rv*
I	*T* 222	4	4	15
II	*T* 259	1	1	31
III	*T* 261	125	125	125
IV	*T* 221	31	62	62
V	*T* 285	62	125	—
VI	*T* 325	125	125	125

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